SPECIFICATION

Title of the Invention

RESIN COATING SOLUTION FOR PLATED STEEL SHEET WITH GOOD ADHESION AFTER PROCESSING AND FABRICATING METHOD OF RESIN-COATED STEEL SHEET USING THE SAME

Brief Description of the Drawings

Fig. 1 is a cross-sectional view of the resin-coated steel sheet for fuel tanks.

Fig. 2 is a diagram showing coating resin on the steel sheet using a coating roll.

Fig. 3 is a diagram of adhesion between phosphoric ester and matrix metal.

* Explanations of main reference numerals in the drawings

1. back-up-roll	2. lift-roll
3. applicator-roll	4. transfer-roll
5. pickup-roll	6. drip pan

Detailed Description of the Invention

The present invention relates to an unleaded plated steel sheet for fuel tanks of an automobile, which substitutes Pb-Sn alloy plated steel sheet (hereinafter referred to as 'terne steel sheet') for fuel tanks of an automobile, more specifically, a resin coating solution for plated steel sheet and a fabricating method using the same, which use unleaded zinc-based alloy plated steel sheet, and control the composition and coating condition of the a resin coating solution and then improves adhesion after processing.

A terne sheet used as a steel sheet for fuel tanks has a problem in scrapping a car since it comprises a large amount of Pb. Instead, unleaded resin-coated steel sheet with

chromated zinc and zinc-based alloy layer has been developed.

The resin-coated steel sheet shows various characteristics according to the material properties of coated resin. Conventionally, phenoxy resin-coated steel sheet has been suggested to improve corrosion resistance and fuel corrosion resistance. However, since the phenoxy resin has a higher glass transition temperature (Tg) than other resins, it has better characteristics such as corrosion resistance and fuel corrosion resistance than epoxy, acryl or urethan resin in a flat plane part which is not subjected to process. However, phenoxy resin has a problem of decreasing corrosion resistance and fuel corrosion resistance due to high glass transition temperature in a processing part during seam processing.

In order to overcome the above problem, there is a way to lower glass transition temperature of phenoxy resin, or to bond phenoxy resin layer and lower chromate layer chemically not to exfoliate the coating and to show good characteristics during seam processing. For example, Japanese Patent Laid Open Publication No. Hei 2-18981 discloses a way to lower glass transition temperature of phenoxy resin and then to modify resin molecules to a rubber, thereby reinforcing a coating adhesion between resin and the lower part which bond thereto. However, if the above method is applied to water-soluble resin, it is difficult to make water-soluble state when modifying it to a rubber, and to add rubber of water-soluble state into phenoxy resin of water-soluble state.

Therefore, the present invention provides a resin coating solution for plated steel sheet and a fabricating method using the same, which are capable of co-mixing resins for lowering glass transition temperature without damaging other material properties of phenoxy resin and have an improved coating adhesion after processing by adding additives for improving coated adhesion between phenoxy resin and matrix metal.

To attain the above object, the invention is derived to a resin coating solution for plated steel sheet having an improved coating adhesion after processing comprising:

(a) an aqueous phenoxy resin solution with the number mean molecular weight of 25,000-50,000;

(b) 2-15 phr of a melamine resin based on the phenoxy resin solution;

(c) 10-20 phr of colloidal silica based on the phenoxy resin solution; and

(d) 5-15 phr of aqueous ethylene-acryl resin comprising 50-80wt% of ethylene and 50-20wt% of acryl resin, with the molecular weight of 20,000-50,000, or 5~15 phr or 0.5-3.0 phr of phosphoric acid-ether based on the phenoxy resin solution.

It is another object of the present invention to provide a method of coating chromated zinc-electroplated steel sheet with a resin coating solution, which has a coating thickness of 2~10μm and an improved coating adhesion after processing after baking drying at 160~250℃.

Preferred embodiments of the invention will be explained with reference to the accompanying drawing.

As shown in Fig. 1, the resin-coated steel sheet according to the present invention has a three-layer structure that zinc or zinc-nickel is plated on a cold-rolled steel sheet and chromate which contains 100mg/m^2 of chrome is treated on the plated steel sheet, and resin solution with good fuel corrosion resistance is coated in the thickness of 2-10μm.

Although zinc-plated steel sheet or zinc-nickel (Zn-Ni) alloy steel sheet can be used as a plated steel sheet, zinc-nickel (Zn-Ni) alloy steel sheet is preferably used in the present invention, because it has better cosmetic corrosion resistance than that of zinc-plated steel sheet.

Chromate solution applied to zinc-nickel plated steel sheet includes a reactive type, electrolyte type and coating type, in which coating type is preferable in terms of cosmetic

corrosion resistance.

Although the chromate solution can be plated on one side or both sides when applied to the steel sheet, it is preferable to be coated on both sides. In case of resin solution, it can be alternatively coated on one side or both sides depending on the needs of consumer to grant functionality. In case of high current condition that is easy for welding and frequent replacing of electrolyte, it is preferable to use steel sheet coated on both sides whereas in case of low current condition and infrequent replacing of electrolyte, it is preferable to use steel sheet coated on one side. When manufacturing a fuel tank by a steel sheet coated with resin on one side, it is preferable to weld the tank by placing the resin coated side to face to fuel side and chromate-coated side which is not coated with resin to face to outer side. Thus, it makes welding easily because the welding electrolyte does not contact with resin part. In addition, if necessary, paint is applied to a side which is not coated with resin in the thickness of about 100 micrometer so as to reinforce corrosion resistance of fuel tank, thereby having little influence on corrosion resistance.

Hereinafter, the resin coating solution of the present invention will be explained in detail.

The resin solution of the present invention is prepared by adding at least one of ethylene-acryl resin or phosphoric ester to phenoxy resin, melamine resin, and colloidal silica, thereby acquiring resin-coated steel sheet with good adhesion after processing.

It is preferable to use a main solution of phenoxy resin having a number average molecular weight of 25,000 to 50,000. When the number average molecular weight is less than 25,000, it is difficult to have desired material properties. When the number average molecular weight is more than 50,000, it is impossible to synthesize the resin due to the limitation of synthetic process.

Phenoxy resin has excellent cosmetic corrosion resistance and fuel corrosion

resistance by the following reasons.

The most characteristic property of phenoxy resin is high glass transition temperature(Tg) which is distinguished from other resins. In case of urethan, epoxy and acryl resin, glass transition temperature of them is around or less than 50℃, although it depends on the molecular weight. However, glass transition temperature of phenoxy resin is 100℃. High glass transition temperature means high movement temperature of resin chain. Thus, since the resin chains do not show Micro Brown movement below the glass transition temperature, they have primary protecting-effect against outer low molecular corrosion element such as moisture or gasoline. That is, if resin chains show Micro Brown movement, the low molecules easily infiltrate between moving chains so that corrosion elements can easily infiltrate. Therefore, resins with high glass transition temperature have screening effect against matrix metal. Particularly, it shows very high screening effect in a flat plane part.

Phenoxy resins, however, have the following shortcomings. That is, since resin coating is very hard, if it is subjected to process, it shows lower drawing than a resin with low glass transition temperature. In addition, since phenoxy resin has a weak adhesion with lower metal coating layer, if it is subjected to process harshly, resin coating is cracked and the adhesion of coating become weaken. Furthermore, if the resin is subjected to process more severe, resin coating exfoliates so that corrosion elements easily infiltrate into the metal coating layer of matrix metal, which results in more corrosion. In manufacturing a fuel tank of an automobile, in order to improve formability during processing, press oil is coated before processing and then the oil is removed. However, the oil removing process makes resin hard. Thus, it cannot expect to have original screening effect because there is damage by the oil removing process in a weak adhesion point. Accordingly, it is preferable to use poly-alloy or poly-blend comprising other resin

with good adhesion and drawing ratio than pure phenoxy resin.

The requirements for the other resin forming poly-blend are as follows: First, it has to have compatibility with water-soluble phenoxy resin not to result in gelation or sludge. Second, it does not have influence to the original excellent characteristics of phenoxy resin such as cosmetic corrosion resistance and fuel corrosion resistance and simultaneously it has to lower glass transition temperature of the whole resin, thereby it improves the coating adhesion.

There are two methods to add ethylene-acryl resin to phenoxy resin. One is chemical method to bond ethylene-acryl resin to phenoxy resin. The other is physical method. The physical method is preferable. Since ethylene-acryl resin used in the present invention is synthesized in gas phase and already water-soluble state, it is impossible to synthesize phenoxy resin of water-soluble state and ethylene-acryl resin of water-soluble state. This is why the chemical method is not appropriate in the present invention.

Ethylene-acryl resin used in the present invention has molecular weight of 20,000~50,000. This includes 50~80% of ethylene and 50~20 % of acryl resin. If acryl resin is comprised less than 20%, it is impossible to make a soluble state whereas, if acryl resin is comprised more than 80%, the glass transition temperature becomes high and adhesion becomes poor. The content of ethylene-acryl resin is preferably 5~15phr. If the content is less than 5phr, coating adhesion effect is less whereas, if more than 15phr, fuel corrosion resistance decreases. Since gasoline is a typical carbohydrate compound of carbon and hydrogen, it has very similar structure to ethylene resin comprising carbon and hydrogen, thus gasoline penetrates into ethylene-acryl resin and then is swelled. This is the reason that the fuel corrosion resistance decreases.

In order to improve coating adhesion of resin, there is a method to introduce

additives other than making poly-blend. The role of additives reinforces adhesion between phenoxy resin and lower chromate layer during seam processing. Mechanism of phosphoric ester of the additive used in the present invention is explained with reference to Fig. 3.

Fig. 3 shows molecular structure of phosphoric ester. Hydroxyl group of phosphoric ester forms hydrogen-bond with hydrogen atom of water molecule, which prevents infiltrating of moisture and improves cosmetic corrosion resistance. Oxygen of phosphoric ester bonds with metal ion of surface layer and improves coating adhesion.

Therefore, it is understood that coating adhesion is improved after processing phenoxy resin due to the complex rising effect with the lowering of glass transition temperature of phenoxy resin itself and combination of metal with phosphoric ester ions.

The content of phosphoric ester is preferably 0.5-3.0phr on the basis of phenoxy resin. If content of phosphoric ester is less than 0.5phr, the effect of adhesion decreases. If content of phosphoric ester is more than 3.0phr, there is no effect according to the increase of amount.

Furthermore, melamine resin as a hardener can be added to the resin solution of the present invention.

The content of melamine resin is 2-15phr on the basis of phenoxy resin. It is preferable to select melamine resin which has high reactivity. If content of melamine is less than 2phr, hardening reaction is not sufficient after resin coating so that desired physical characteristic is not obtained. On the contrary, if content of melamine is more than 15phr, reactions between hardeners themselves occur so that it adversely influences to the physical characteristics of coating layer.

Further additive added to the resin solution of the present invention is colloidal silica. Colloidal silica is added to improve cosmetic corrosion resistance of resin. The

content of colloidal silica is preferably 10-20phr on the basis of phenoxy resin content. If the content of colloidal silica is less than 10phr, it is too little to have cosmetic corrosion resistance effect. On the contrary, if content of colloidal silica is more than 20phr, there is no improved effect of cosmetic corrosion resistance relative to the added content of colloidal silica.

Hereinafter, a method of fabricating resin-coated steel sheet using resin solution of the present invention is explained.

The resin-coated steel sheet of the present invention is manufactured by treating chromate on zinc or zinc alloy plated steel sheet, baking drying, coating resin solution and baking drying the steel sheet.

Thickness of the resin coating which is coated on upper side of chromate layer is preferably 2.0-10.0μm. If the thickness is less than 2.0μm, the thickness of the coating is too thin to have sufficient cosmetic corrosion resistance and fuel corrosion resistance. On the contrary, if the thickness is more than 10.0μm, there is no influence to cosmetic corrosion resistance and fuel corrosion resistance according to increase of the thickness as well as weldability decreases.

Baking temperature after coating the resin solution is preferably 160-250℃ based on metal temperature(MT). If baking temperature is less than 160℃, hardening reaction of the resin is not sufficient to have cosmetic corrosion resistance and fuel corrosion resistance. On the contrary, if the baking temperature is more than 250℃, hardening reaction does not occur any longer and loss of calories increases.

Coating processes of steel sheet include roll coating, spray, impregnation and so on. It is preferably to use roll coating process in the present invention. Fig. 2 shows roll coating equipment used for treating chromate and coating resin solution. The coating process as shown in Fig. 2 comprises dipping resin in a drip pan into pick-up-roll(P.U.R),

transferring it by a transfer-roll(T.F.R), dipping it into steel sheet in the applicator-roll(A.P.R), and drying in the oven. The amount of resin attached to the steel sheet is regulated by each roll driving direction, rolling speed, and each roll adhesion pressure.

In the present invention, the above roll coating process can be applicable to one side or both sides of steel sheet.

Now, preferred embodiments are suggested to help the apparent understanding of the present invention.

Example 1

A composition of phenoxy resin with number average molecular weight of 50,000, 5phr of melamine resin as a hardener, 15phr of colloidal silica with particle size 20nm and 2phr of wax is referred to as a standard solution composition unless other specific note. In addition, the following method is referred to as a standard method of manufacturing steel sheet: treating chromate on electric zinc and zinc alloy plated steel sheet with plate amount of $30g/m^2$, baking drying so as to make metal temperature of 160℃, cooling it, coating resin solution prepared by various composition, baking drying so as to make metal temperature of 190℃, and forming resin-coated steel sheet with dried coating thickness of 3㎛.

After preparing resin solution by mixing ethylene-acryl resin of which weight ratio is 80:20 of ethylene to acryl with the above standard solution according to the content of below table 1, the resin-coated steel sheet was manufactured by coating the resin solution on the steel sheet plated with zinc of $20{\sim}30g/m^2$ and treated with chromate of $100mg/m^2$ by roll-coating process, baking drying so as to make metal temperature of 190℃, water-cooling and forming resin-coated steel sheet with dried coating thickness of 3 ㎛.

The cosmetic corrosion resistance of the steel sheet prepared by the above process

was measured in a processing part by using a salt spray test. A specimen for measurement was prepared by cutting flat plane into 95mm, preparing a cup with diameter of 50mm and height of 25mm, taking out the cup from salt spray after 500 hours, washing with distilled water and drying. According to the amount of occurrence of rust, the grades of cosmetic corrosion resistance were classified in the following way and table 1 showed the result.

Circle in circle (◎): The area of occurrence of white rust is 5% or less with respect to the total area of a specimen.

Circle (○): The area of occurrence of white rust is in the range of 5-30% with respect to the total area of a specimen.

Square (□): The area of occurrence of white rust is in the range of 30-50% with respect to the total area of a specimen.

Triangle (△): The area of occurrence of white rust is in the range of 50-100% with respect to the total area of a specimen.

In addition, in order to measure coating adhesion after processing, two types of mode were used. The first mode was to measure exfoliated area of resin after detaching cellophane tape that was attached to around of cup specimen with diameter of 50mm and height 25mm cut from flat plane of 95mm. The second mode was to measure the same method as the first mode after applying ultrasound to 10% caustic soda solution for 3 minutes at 50℃ and washing. Then, coating adhesion was measured according to the below grades and table 1 showed the result.

Circle in circle (◎): The exfoliated area is 0%.

Circle (○): The exfoliated area is 1-5%.

Square (□): The exfoliated area is 5-10%.

Triangle (△): The exfoliated area is 10-20%.

X: The exfoliated area is more than 20%.

Fuel corrosion resistance was measured as follows: A flat plane facing to fuel is cut into 95㎜, and formed to cups with diameter of 50㎜ and height of 25㎜. Three kinds of solution of 25ml were poured into the cups. Thereafter, the opening portions of the cups were covered with transparent glass plates by interposing circular "O" rings and fixed with clamp to prevent gasoline from leaking. The solutions were classified into A type, B type and C type. For the A type solution, regular gasoline was mixed with 5% of sodium chloride (NaCl) aqueous solution. For the B type solution, regular gasoline was mixed with 0.2% of sodium chloride. For the C type solution, 85% of regular gasoline was mixed with 14% of methanol and distilled water containing 60ppm of formic acid and 20ppm of Cl- ion. In order to simulate driving situation of automobile, rocking equipment was used such that the solution contained in the cup was in rocking motion. The cups were allowed to stand for 4 months. Then, the cups were taken out, washed by distilled water, and dried. According to the amount of occurrence of rust, the grades of fuel corrosion resistance were classified in the following way and table 1 showed the result.

Circle in circle (◎): The area of occurrence of white rust is 5% or less with respect to the total area of a specimen.

Circle (○): The area of occurrence of white rust is in the range of 5-30% with respect to the total area of a specimen.

Square (□): The area of occurrence of white rust is in the range of 30-50% with respect to the total area of a specimen.

Triangle (△): The area of occurrence of white rust is in the range of 50-100% with respect to the total area of a specimen.

X: Red rust occurred.

Table 1

<table>
<tr><th rowspan="2">Ex. No.</th><th>Main solution</th><th colspan="2">Additive</th><th colspan="2">hardener</th><th colspan="3">Qualification measurement after processing</th></tr>
<tr><th>Type</th><th>Type</th><th>content</th><th>Type</th><th>content</th><th>Coating adhesion</th><th>Cosmetic corrosion resistance</th><th>Fuel corrosion resistance</th></tr>
<tr><td>Com.Ex.1</td><td rowspan="18">Phenoxy resin</td><td rowspan="18">Ethylene-acryl resin</td><td rowspan="3">0</td><td rowspan="18">Melamine resin</td><td>5</td><td rowspan="2">□</td><td rowspan="2">○</td><td rowspan="3">○</td></tr>
<tr><td>Com.Ex.2</td><td>10</td></tr>
<tr><td>Com.Ex.3</td><td>15</td><td>△</td><td>□</td></tr>
<tr><td>Com.Ex.4</td><td rowspan="3">3</td><td>5</td><td rowspan="3">○</td><td rowspan="15">◎</td><td rowspan="3">◎</td></tr>
<tr><td>Com.Ex.5</td><td>10</td></tr>
<tr><td>Com.Ex.6</td><td>15</td></tr>
<tr><td>Com.Ex.7</td><td rowspan="3">20</td><td>5</td><td rowspan="12">◎</td><td>□</td></tr>
<tr><td>Com.Ex.8</td><td>10</td><td rowspan="2">○</td></tr>
<tr><td>Com.Ex.9</td><td>15</td></tr>
<tr><td>Ex.1</td><td>5</td><td rowspan="3">5</td><td rowspan="9">◎</td></tr>
<tr><td>Ex.2</td><td>10</td></tr>
<tr><td>Ex.3</td><td>15</td></tr>
<tr><td>Ex.4</td><td>5</td><td rowspan="3">10</td></tr>
<tr><td>Ex.5</td><td>10</td></tr>
<tr><td>Ex.6</td><td>15</td></tr>
<tr><td>Ex.7</td><td>5</td><td rowspan="3">15</td></tr>
<tr><td>Ex.8</td><td>10</td></tr>
<tr><td>Ex.9</td><td>15</td></tr>
</table>

The above table 1 shows the result of measurement according to the various contents of ethylene-acryl resin as an additive and melamine resin as a hardener. As can be seen in table 1, when content of ethylene-acryl resin is more than 20phr, coating adhesion and cosmetic corrosion resistance are good but fuel corrosion resistance

decreases. In addition, when ethylene-acryl resin content is less than 5phr, the comparison examples show inferior characteristics to the examples of the present invention.

Example 2

After preparing resin solution by mixing phosphoric ester as an additive with the above standard solution according to the content of below table 2, the resin-coated steel sheet was manufactured by coating the resin solution on the steel sheet plated with zinc of 20~30g/m^2 and treated with 100mg/m^2 of chromate by roll-coating process, baking drying so as to make metal temperature of 190℃, water-cooling and forming resin-coated steel sheet with dried coating thickness of 3μm. After measuring same as Example 1, the result was shown in table 2.

Table 2

<table>
<tr><th rowspan="2">Ex. No.</th><th>Main solution</th><th colspan="2">additive</th><th colspan="2">hardener</th><th colspan="3">Qualification measurement after processing</th></tr>
<tr><th>Type</th><th>Type</th><th>content</th><th>Type</th><th>content</th><th>Coating adhesion</th><th>Cosmetic corrosion resistance</th><th>Fuel corrosion resistance</th></tr>
<tr><td>Com.Ex.A</td><td rowspan="18">Phenoxy resin</td><td rowspan="18">Phosphoric ester</td><td rowspan="3">0.3</td><td rowspan="18">Melamine resin</td><td>5</td><td rowspan="2">□</td><td>○</td><td rowspan="5">◎</td></tr>
<tr><td>Com.Ex.B</td><td>10</td><td rowspan="2">□</td></tr>
<tr><td>Com.Ex.C</td><td>15</td><td>○</td></tr>
<tr><td>Com.Ex.D</td><td rowspan="3">4.0</td><td>5</td><td rowspan="15">◎</td><td rowspan="15">◎</td></tr>
<tr><td>Com.Ex.E</td><td>10</td></tr>
<tr><td>Com.Ex.F</td><td>15</td><td>○</td></tr>
<tr><td>Ex.A</td><td>0.5</td><td rowspan="4">5</td><td rowspan="12">◎</td></tr>
<tr><td>Ex.B</td><td>1.0</td></tr>
<tr><td>Ex.C</td><td>2.0</td></tr>
<tr><td>Ex.D</td><td>3.0</td></tr>
<tr><td>Ex.E</td><td>0.5</td><td rowspan="4">10</td></tr>
<tr><td>Ex.F</td><td>1.0</td></tr>
<tr><td>Ex.G</td><td>2.0</td></tr>
<tr><td>Ex.H</td><td>3.0</td></tr>
<tr><td>Ex.I</td><td>0.5</td><td rowspan="4">15</td></tr>
<tr><td>Ex.J</td><td>1.0</td></tr>
<tr><td>Ex.K</td><td>2.0</td></tr>
<tr><td>Ex.L</td><td>3.0</td></tr>
</table>

The above table 2 shows the result of measurement according to the various contents of phosphoric ester resin as an additive and melamine resin as a hardener. As can be seen in table 2, when content of phosphoric ester resin is in the range of 0.5-3.0phr,

coating adhesion after processing is improved. However, when phosphoric ester content is more than 3.0phr or less than 0.5phr, the comparison examples show inferior characteristics to the examples of the present invention.

Meanwhile, when both phosphoric ester and ethylene-acryl resin as additives are mixed to the resin solution of the present invention, it shows the same or excellent effect than that of each additive is mixed as the above examples.

As described above, by fabricating resin coating solution in which ethylene-acryl resin and phosphoric ester are added to the water-soluble phenoxy resin, newly unleaded plated steel sheet for a fuel tank with better adhesion after processing, fuel corrosion resistance, and corrosion resistance is provided. Therefore, the present invention predominating over conventional Pb-Sn plated steel sheet is harmony with the environment. In addition, according to the present invention, it is possible to improve the quality of the steel sheet and break up the dissatisfaction of the consumers.